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Experimental researches on "Wetting effect" and "Liquostriction"

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With 31 figures in the text

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1. Introductory

Starting from the fact that the mineral mica is more easily splitted in the presence of water than in a dry condition (1)[1], experiments supported by Messrs Uddeholms AB, were made by C. Benedicks and G. Ruben (2), (3), (4) and proved this "wetting effect" to be a phenomenon of considerable practical importance.

The instigation to these experiments was the failure of some large bolts submitted to the Metallographic Institute for investigation. The conclusion tentatively drawn was that the fractures were connected with the presence, on the surface of the bolts, of condensed water (from an inlet of fresh air). A few traction experiments showed, that fracture occurred in recently wetted notches much easier than in dry notches.

In order to check this astonishing result, an industrial laboratory (ASEA) had carried out some series of fatigue tests (1933, 1938): a non-rusting steel (13 % Cr) actually showed a strength diminution of 40 to 60 %, when the specimens were wetted with water (instead of oil). A carbon steel of the same composition as the broken bolts showed a strength decrease of 40 to 50 %. In order to eliminate the possibility of corrosion — near at hand to suspect — the experiments then made by C. Benedicks and G. Ruben (2 b) were in first line performed on homogeneous glass. Quenched steel was then investigated. For both, the wetting effect corresponded to a *decrease* of the tensile strength ("negative effect") or to an *increase* ("positive effect"). The wetting effect was found to be particularly strong *in zinc*, wetted by zinc-saturated mercury.[2] For the determinations use was made of a Chevenard micromachine, available thanks to the courtesy of Jernkontoret.

2. New experiments regarding the wetting effect

a. Lump-sugar

The phenomenon starting in the very surface of the solid, it seems necessary that it should appear likewise in a porous body. (Frequently, the necessary specimens are easier to produce than in solid bodies.)

On account of this, some experiments were made on lump-sugar. The specimens used, having the dimensions 27 × 12 × 6.2 mm, were placed on two edges 14 mm distant; the loading was made centrally using a steel cylinder ($r = 4$ mm) and small shots.

"Sugar I" was rather pure (prewar quality); "Sugar II" was less well refined. The liquids used — sugar solution in water as well as other liquids — were carefully saturated with the sugar concerned, using a shaking machine. The determinations of surface tension were carried out by means of a capillary plate method.

The wetting effect was found to be a very marked one, corresponding for an aqueous sugar solution to a *considerable reduction of the bending strength.* For Sugar I this reduction amounted to 75 % (Fig. 1), while Sugar II even gave a reduction of 84 % (Fig. 2). (The bending strength of Sugar I corresponded to a load of 2.0 kg, that of II to 3.4 kg.)

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[1] The useful influence of water for the splitting of mica was known as early as 1892: Lewis Wright, Light. New York 1892, p. 289. (See J. Strong, Modern Physical Laboratory Practice. London a. Glasgow 1944, p. 389.)

[2] (2 b) p. 58; (4) p. 12.

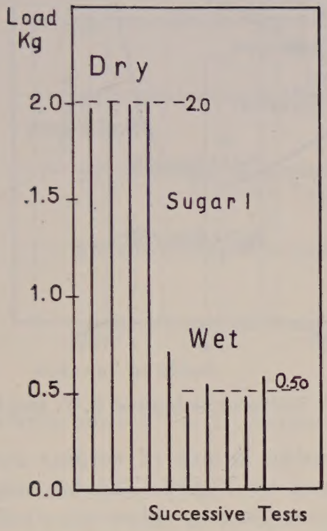

Fig. 1. Wetting effect in Sugar I; Saturated aqueous sugar solution. Reduction of strength 75 %.

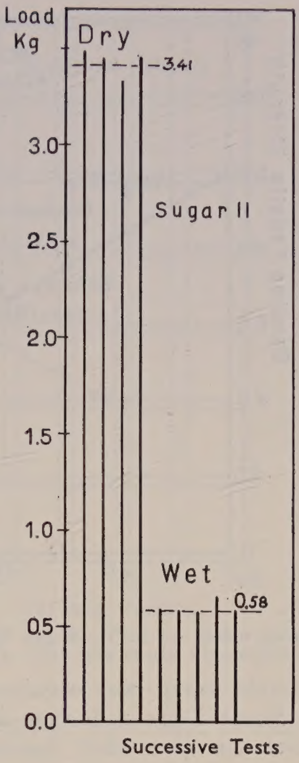

Fig. 2. Wetting effect in Sugar II; Saturated sugar solution. Reduction 84 %.

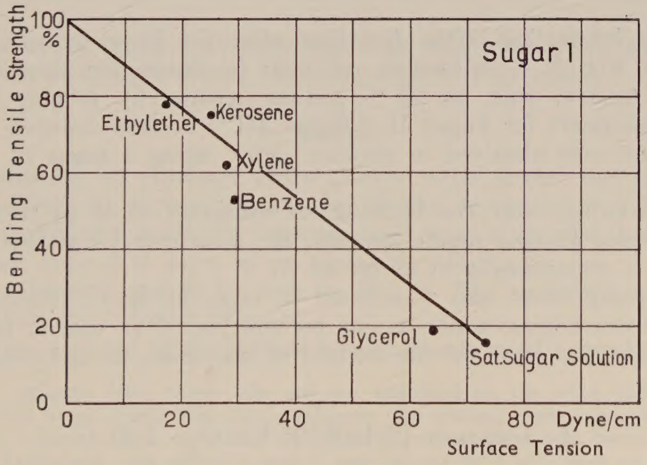

Fig. 3. Wetting effect — Surface tension (S.T.), Sugar I. Strength decreasing with increasing S. T. (Liquids saturated.)

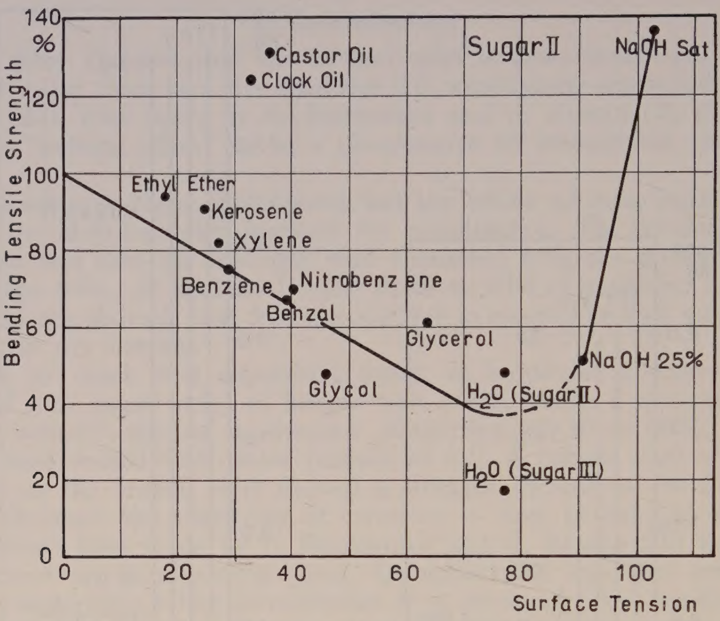

Fig. 4. Wetting effect — S. T., Sugar II. Strength increases at highest S. T. and for fat oils.

A noticeable result was obtained when using liquids of *varying surface tensions.* For Sugar I the reduction is evidenced by Fig. 3. The lowering is sensibly a linear one (for ether, kerosene, xylene, benzene, glycerol, aqueous sugar solution).

For Sugar II (with some other liquids) the remarkable result was that shown by Fig. 4. (It may be observed incidentally, that nitrobenzene and benzal, possessing the same surface tension, show almost exactly the same percentic reduction.)

Particularly interesting is the fact that after the linear portion of the curve — similar to Fig. 3. — a *bending off may be drawn for liquids with a very high surface tension,* such as 25 % sodium hydroxide. It may be remarked, that the lower point for Sugar II ("Sugar III") is that deduced from Fig. 2; the upper one was obtained in another series, using a sugar of probably another purity.

It is remarkable, that the bending off continues so as to represent finally *an increase of the bending tensile strength.* So, a saturated NaOH-solution (about 40 %) causes a *strengthening* of about 38 %.

A strengthening effect also was found to occur for fat oils (Castor oil, "Clock oil"). The strengthening action might be interpreted as caused by the formation of an *adsorbed layer* on the surface of the solid, as assumed in the case of lubrication.

b. Gypsum ("chalk"); $CaSO_4 \cdot 2\ H_2O$

Some tests were made on common white drawing "chalk" (composition found actually to be 93.5 % $CaSO_4 \cdot 2\ H_2O$, with some organic binding medium.

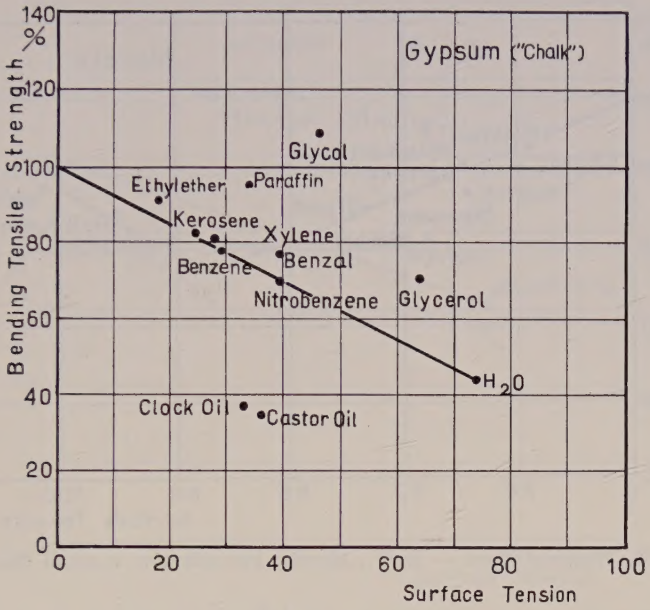

Fig. 5. Wetting effect — S. T., Gypsum ("chalk"). (Fat oils cause abnormally strong decrease.)

The results obtained (Fig. 5) were less regular than say, in Fig. 3, but a straight line may serve as a first approximation.

The most striking fact concerned the fat oils: castor oil and "tower clock oil" caused no strenghtening of the solid, as was the case for sugar; instead a strong weakening action was found to occur.[1]

This action much differs from the one which was found to occur for paraffin oil (Fig. 5).[2]

It may be added, that tests were made as well with water saturated with the "chalk", as with pure water; the difference is very small.

c. Marble

Some experiments on (Italian) white marble were carried out in the Chevenard micromachine. As a rule, the section of the specimens was 5.0 × 9.5 mm. They were prepared by a slowly rotating, well wetted circular steel saw (80 × × 0.8 mm), and kept 2–3 days in an exsiccator (H_2SO_4).

The figures obtained are to be seen in Fig. 6. The spreading appears to be sligthly less than for "chalk" (Fig. 5).

It will be seen, that up to the surface tension of saturated water (72.3 dyne/cm),

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[1] This would indicate that these oils are *not* adsorbed on the solid body as might be the most frequent case. From this the conclusion was drawn, that a fat oil does not act as a lubricator between two pieces of "chalk". This conclusion was found to hold true: some castor oil interposed was actually found more to *act as a glue than as a lubricator.*

[2] This induced the conclusion that paraffin oil might have some tendency of lubricating the "chalk". It was actually found that it at least does not exert any gluing action whatever. These questions no doubt *merit a* close examination.

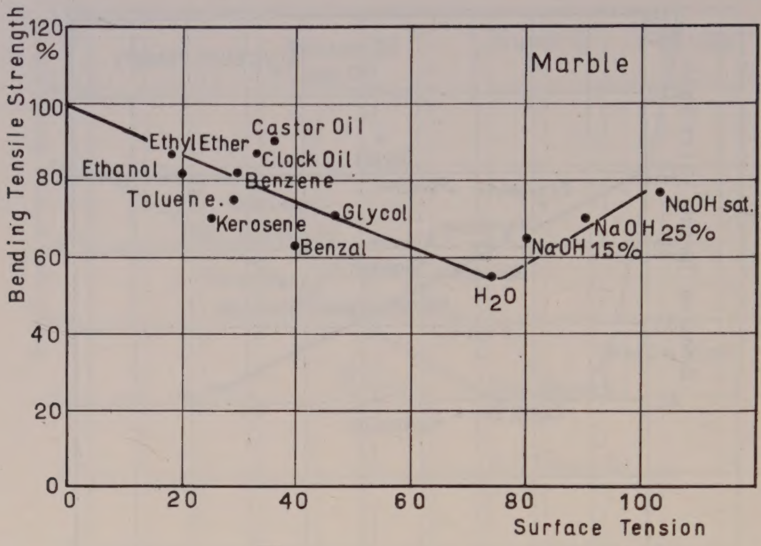

Fig. 6. Wetting effect — S. T., Marble. Fat oils give a small decrease.

the decrease with some approximation follows a straight line. Thereafter an increase occurs, as was the case for sugar II (Fig. 4).

The fat oils do not cause any strengthening as in the case of sugar (Fig. 4), though they are situated beyond the straight line (going through H_2O). The following values (NaOH) are likewise increasing.

d. Comparison with the previous experiments on glass

In the basic researches on the wetting effect (2 b) it was pointed out, that the weakening ought to be particularly strong in the case of wetting liquid possessing high attractive forces, as mercury. High attractive forces imply a *high surface tension.* Hence it might have been natural to expect the weakening effect to increase in parallel with the surface tension. For the weakening liquids used (ethanol, turpentine, glycerol and water) it is actually seen that the *weakening increases with increasing surface tension*: Fig. 7[1]).

As was the case in Fig. 4, a bending off may be said to occur for the liquid with the highest surface tension (10 % sodium hydroxide).

Interesting is the occurrence of strengthening liquids: in first line "tar oil", which causes a strengthening of 30 %; its surface tension cannot be given. Further, kerosene (petroleum) and also toluene exert a strengthening action.

This proves that the phenomena which occur on wetting are fairly complicated.

e. Comparison with the experiments on quenched steel

Rather similar results were those obtained on quenched steel (Fig. 8[1]). Ethanol, octanol, carbon tetrachloride and water are seen to lay rather near a straight

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[1] The surface tensions used here are table values; they may be considered as sufficiently accurate. The figures below 100 % are taken from Tab. III in (2 b), as they do not occur in the final Tab. VII. Hence, the comparison may only be an approximate one.

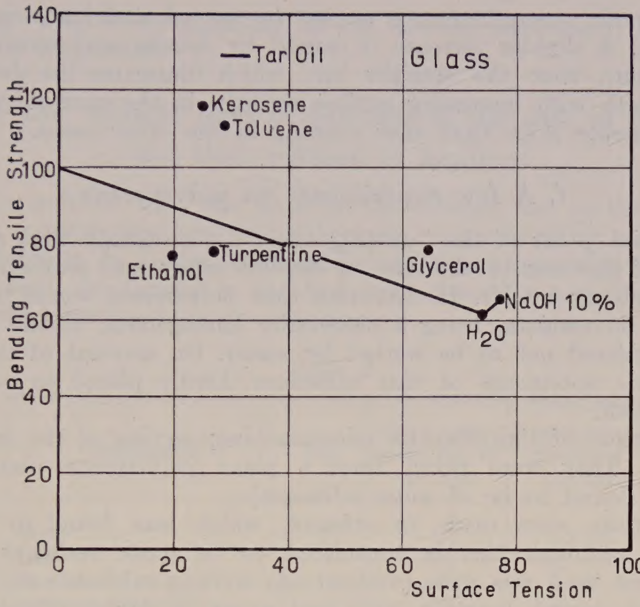

Fig. 7. Wetting effect — S. T., Glass (C. B. & G. R.) Tar oil, Kerosene . . . increase strength.

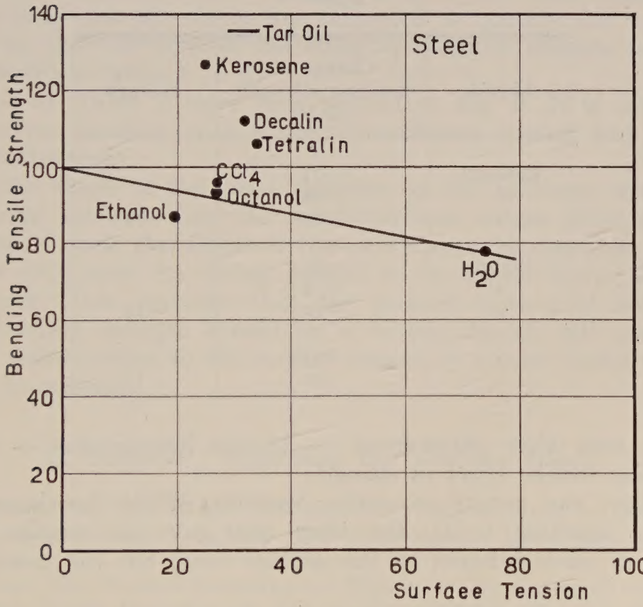

Fig. 8. Wetting effect — S. T., Quenched steel (C. B. & G. R.). Tar oil, Kerosene increase strength.

line. Considerable strengthening is caused by tar oil and kerosene, as was the case for glass. A slighter increase is caused by decalin and tetralin.

It is obvious, that the straight line which illustrates the decrease of the bending strength with increasing surface tension, in the case of quenched steel, possesses a smaller slope than that existing in the other cases.

f. A few experiments on polystyrene

The essential point of the "wetting effect" is obviously that a *true wetting takes place.* If this not be the case, a sensible effect may scarcely be expected. It was pointed out by Mr. H. LIANDER that polystyrene would be particularly interesting to investigate, being a chemically homogenous, brittle substance — which is considered not to be wetted by water. On account of this, tests were made on some specimens of this substance, kindly placed to our disposition by Mr. LIANDER.

Use was made of CHEVENARDS micromachine; section of the specimens was 9.5 × 3.0 mm. They were taken from a plane polystyrene plate (its rolling direction was found to be of some influence).

The first tests were made in ethanol, which was found to wet well the substance — although this is considered to be quite resistant to ethanol.[2] The water then used was pure (without any wetting substance such as tergitol).

The contact period between solid and water no doubt influences, but was not investigated in detail.

Wetting effect in polystyrene

Table 1

Liquid	Change of bending strength in %	Average
Ethanol	−77	
»	−69	
»	−77	−74
Water	−24	
»	− 5	
»	−13	−14
»	+13	
»	+20	+16

It will be seen that polystyrene — though homogenous — shows a *very strong decreasing wetting effect in ethanol.*

As for water, the results are rather variable. While the three first experiments gave a decrease (−14), the later ones gave an increase (+16). This might stand in some relation to the contact time, but the tests are too few

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[1] (2), p. 97.

[2] C. D. HODGMAN, Handbook of Chem. a. Physics. Cleveland, Oh. 1947, p. 1296; F. PABST, Kunststoff-Taschenbuch, 5. Aufl., Berlin-Dahlem 1940, p. 84.

to allow any definite consequence to be drawn, particularly on account of the anisotropy mentioned.

g. Slope of the straight lines of decrease in the case of various solids and their relation to hardness

As already pointed out, the slope of the straight line in the case of hardened steel is considerably less than otherwise. A quantitative comparison possesses much interest. In *Table 2* are compiled the slopes appearing for the different substances tested; the figures in the 3 rd column are those read off (in percent) at an (arbitrary) surface tension = 70 dyn/cm.

Table 2

Substance	Fig.	Slope parameter for 70 dyn/mm	Approximate hardness (Mohs)
Steel	8	−21	8.5—5
Glass	7	−36	6.5—4.5
Marble	6	−43	4—3
Gypsum ("chalk")	5	−53	2—1.6
Sugar II	4	−60	(2—1)
» I	3	−80	(1.5—1)

In this table, the limits of Mohs *hardness* have also been introduced.[1]

It will be seen that the slopes are subjected to considerable variation. The striking fact is, that *the order of the slopes is found to coincide with the inverse order of the hardness values.*[2]

The figures of Table 2 have been plotted in Fig. 9. It is easy to draw a continuous curve, starting with a nearly rectilinear portion and then slightly bending off horizontally.

Obviously the shape of the curve depends on the arbitrary scale introduced by Mohs; being known, that the small hardness values differ relatively less than the higher ones, the shape of the curve appears plausible. Further, the hardness of a solid must be closely related to its *surface tension* or to its inner attractive forces. This involves that the present method of determining the decrease of bending strength caused by a wetting liquid, will probably render possible the *determination of the surface tension of a solid,* hitherto considered to be rather inaccessible.

h. Summary regarding the wetting effect

1. In addition to the earlier wetting effect experiments — particularly on glass and quenched steel — a few new experiments have been performed on

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[1] C. D. Hodgman, Handbook of Chemistry and Physics. 30. Ed. Cleveland, Oh. 1947, p. 1715.

[2] The hardness figures for sugar are only roughly estimated. The fact that Sugar II is considerably harder than Sugar I is in harmony with the tensile strength, as seen in Figs. 1 and 2.

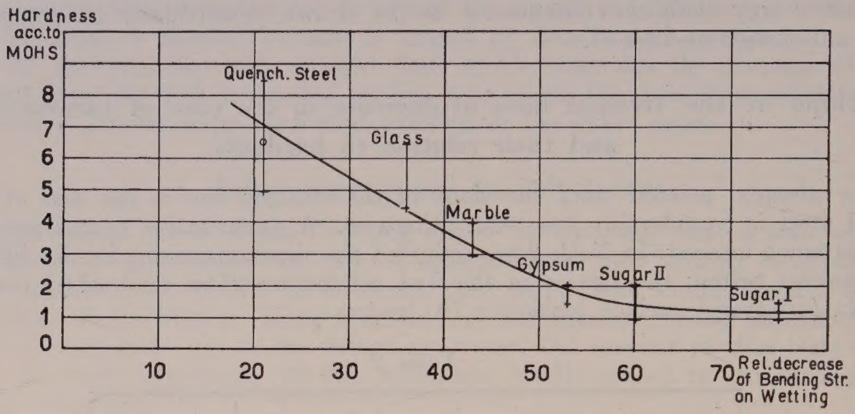

Fig. 9. Relation between rel. decrease of bending strength and hardness.

various softer substances, viz. polystyrene, lump-sugar, gypsum ("chalk") and marble.

2. As for polystyrene — known as hardly being wet by water, which would exclude a sensible "wetting effect" — it has been established that ethanol — actually wetting this substance — causes a considerable wetting effect, amounting to a decrease of 74 %. Water proved to present great irregularities, apparently causing an increase as well as a decrease of the bending strength.

3. Sugar I (purest) gave a strikingly linear relation between decrease of bending tensile strength and surface tension of the (saturated) liquids (Fig. 3).

Sugar II (less pure) gave quite a similar straight line (with a smaller slope), but showed certain complications (strengthening), probably due to adsorption of polar liquids (Fig. 4).

4. Straight lines were also obtained for gypsum ("chalk") and marble (Fig. 5, 6).

The slopes of the straight lines, i.e. the relative decrease of the bending strength of the substances, have been plotted against a *hardness parameter*; thereby use was made of the MOHS hardness figures (Fig. 9). It is obvious that *a relation exists between the relative decrease of bending strength and the hardness parameter.*

As the hardness must be closely related to the surface tension of the solid, the conclusion is near at hand, that the present method might afford a *possibility of determining the surface tension of a solid body.*

5. The observations carried out (see Fig. 4) prove that the wetting action of liquids on a solid may be of two different kinds: 1. those *decreasing* the bending strength, generally following a straight line. 2. Those *increasing* the bending strength might be located on an upwards curved line, or in other more or less irregular way.

The first group seems to correspond to those ("nonpolar") liquids, where ANTONOFFS *law* (13) is valid, while the second group might have a "polar" character — and might form exception to this law.

3. Theoretical points of view

i. Character of the conception surface tension

Already earlier some attempts were made to explain the phenomena shown by the wetting effect theoretically. (2 b, 3). A new conception was then advanced regarding the character of the *surface tension* (5). The main points are the following.

The conception "molecular sphere of activity", introduced by LAPLACE (1805), is used in most text-books even nowadays for deducing the existence of *surface tension*: for a particle in the surface, only the half of the molecular sphere exists, giving a resultant attracting force perpendicular to the surface (see for instance J. J. BIKERMAN (6)). As well known, the surface tension exerts its activity *in the surface*. Hence, a force perpendicular to the surface is scarcely suitable for its deduction. The molecular sphere of activity may have been a useful conception[1]; as compared with present ideas, it possesses a subordinate interest.

Let us now accept the following assumptions:

1. The attractive forces may be considered to behave as elastic lines (the "lines of force", as used by FARADAY, gave a perspicacity not reached otherwise).
2. Fundamental for the atomic nucleus is, according to present ideas, its *mass*. This results from a nucleus being composed of neutrons and protons (nucleons). From each nucleon a definite number (n) of unitary attractive forces may be supposed to emanate (characteristic for mass is to attract mass!).
3. Hence, from every atomic nucleus, composed by a definite number (N) of nucleons, a definite number (nN) of unitary attractive forces may be assumed to emanate.
4. Every line of force emanating from a nucleus is supposed to continue to another (neighbouring) nucleus. (This in analogy to the valency forces as generally assumed).
5. The lines of force emanating from a nucleus are regularly distributed around certain preferential directions in space ("bunches of force").

In order to substantiate our conceptions, a regular arrangement of the atoms in a condensed phase may first be admitted. We suppose a two-dimensional quadratic nuclear lattice to exist.

The points in the lattice represent merely mean positions of the nuclei of a dynamic lattice. Let us admit that from every nucleus 4 × 6 lines of force do emanate. Let us draw a symbolic scheme of the network of forces occurring near a boundary surface (beyond which no atoms are supposed to exist).

It would be near at hand to assume a scheme as that of Fig. 10 a, indicating that the lines of force of the surface nuclei continue *in infinitum*.

This, however, is contrary to the above point 4; these lines of force must have the possibility of uniting themselves with the lines of force from the neighbouring nuclei, as shown by Fig. 10 b. If this be the case, the attraction between neighbouring atoms in the surface will be an increased one. According to the symbolic figures, the increase will be from "6" to "9" lines of force. We might compare this increase with that resulting from a *double binding*, as assumed in organic chemistry since KEKULÉ.

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[1] It has been evaluated for a number of metals by C. BENEDICKS (7).

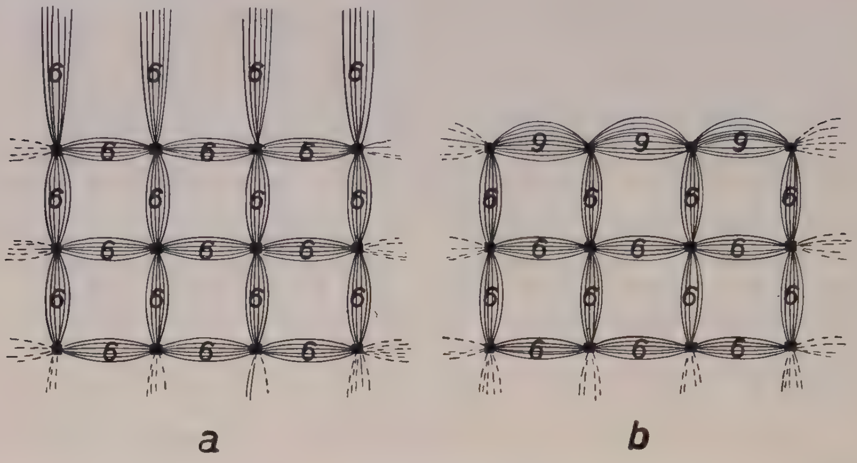

Fig. 10. Elucidation of the nature of surface tension. *a* symbolic exposition of the nuclear bindings in a condensed phase. — *b* illustrates that the bindings are stronger in the free surface than in the interior.

This surplus of attracting forces ("9" instead of "6") occurring in the free surface may be said to be a clear expression of the *import of the conception surface tension.*

In fact we have merely considered a two-dimensional, quadratic lattice, but the reasoning will be quite the same for a three-dimensional one, and also for other kinds of regular lattices. Finally, no difference in the reasoning arises if the arrangement of the atoms is an irregular one, as supposed in ordinary liquids.

These considerations show: *if in a condensed system of atoms there is a free boundary surface, this surface will possess a definite surplus of attracting forces.*

It is frequently said that the surface of a condensed phase behaves as if an *elastic film was acting there* (an assumption for which is carefully warned!). We have seen, however, that a quite particular *surplus of forces ought to occur in the free surface.*

j. Basic conclusions

From this, we may draw some important conclusions.

If to a solid body *foreign atoms* are supplied by wetting with a "normal" liquid, then

A. the surface tension of the solid body must be lowered (say from "9" towards "6", or from the state Fig. 10 b in the direction towards Fig. 10 a).

This signifies a *lowering* of the bending tensile strength: as a matter of fact, the greater the surface tension of a solid, the greater the bending strength is to be expected. This affords a simple explanation of the weakening "*wetting effect*".

As for the *strengthening wetting effect* the nearest explanation might be that the liquid causes an increase of the surface tension, say in forming an adsorbed thin film on the solid surface ("a monomolecular layer"), but other explanations may also be possible (if considering the presence of surface fissures and their eventually increased cohesion when being filled by a wetting liquid).

B. This lowering of the tensile strength may be expected in first line to *increase with the surface tension of the liquid.*

This has *actually been proved by the above experiments*: The decreasing strength lines in Figs. 3, 4, 5, 6, as likewise the earlier experiments on steel and glass, in Figs. 7, 8, clearly express this law.

C. The presence of a wetting liquid, causing the attracting forces situated in the surface to decrease (say from "9" towards "6"; Fig. 10 b) leads to an important conclusion: *the presence of the liquid must cause an expansion of the solid body.* As a matter of fact, the thermal agitation of the atoms (leading to collisions!) will result in an increased distance, provided the attractive forces decrease.

This effect — so far unknown — may be designated as "*liquostriction*"; it will be investigated in order to establish its existence or not.

D. It must be expected that this "liquostriction" if existing will increase with the surface tension of the liquid, as has been found to be the case for the wetting effect. This problem also must be investigated.

The conclusions C and D have been experimentally tested and were found to be supported by the experiments.

Preliminar communications have been given (5) (8) (9) (10).

In the following, the experimental arrangements used will be described in some details, with some desirable controlling work.

4. Experiments regarding "Liquostriction"

k. Experimental arrangement used

The changes of length to expect being fairly small, the measurements were made using a *mikrokator* (Type 220 A, No. 7766) kindly placed at disposal by Messrs. AB. C. E. Johansson, Eskilstuna.[1] The arrangement used is to be seen in Fig. 11. The wire A to be investigated at the one end is fixed in a metal rod B, carried by a marble block C, which rests on a marble table. The other end of A is fixed in the vertical arm D of an angular piece, carried by ruby bearings and outbalanced by screwed weights E and F. The ruby bearings are mounted in an iron stand H, solidly fixed to the table I of the mikrokator. The horizontal arm G is connected (generally by means of a quartz fiber) with the hook K of the mikrokator. One scale division corresponded to $0.1 \cdot 10^{-3}$ mm (pointer moving from 0 — right hand — to 80). The adjustable tension f was generally used between 2 and 15 g (possible maximum 125 g). In the present instrument, the tension f is obtained by a combination of mechanical and magnetical devices.

The dimensions of the quartz and other fibres were 0.03–0.05 mm in diameter and 210–250 mm in length. The temperature averaged + 20° C. The tension used — intented to have a strictly constant value — was obtained in suspending a suitable weight on the hook K and turning the provided adjusting screw so that the pointer approached a mean position.

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[1] As for the construction of the instrument, see a paper by its inventor: H. Abramson (11).

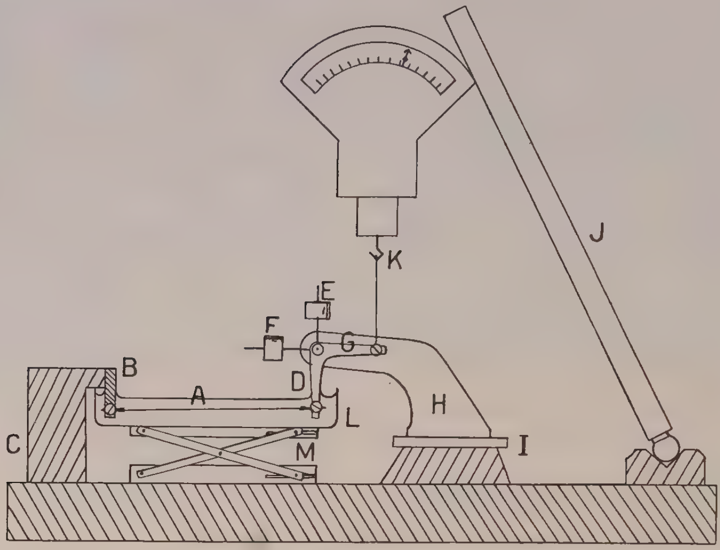

Fig. 11. Apparatus arrangement used for the determination of liquostriction.

L is a vessel of brass containing the liquid to be used; it may be raised or lowered (suitable stoppers!) by means of the adjustable table M (governed by thin iron rods).

L contains an electrically heated thermostate wire. As in most preliminary trials quartz fibre was used, the temperature control was, at first, not very exacting. Thermocouple measurements showed variations not surpassing ± 0.2° C.

The liquid, being subjected to some evaporation, becomes slightly cooler than the wire (air temperature); it was found easy, on using a weak current in the thermostate-wire (0.18 amp.; resistance = about 20 ohms) to compensate for the evaporation heat.

Much work was consecrated to the problem of realizing an automatic equalization of the temperature of the liquid and that of the adjacent air, but the success was not good (Cp. p. 424).

It may be added that the primary adjustment of the pointer was found to be easily realized by means of weak lateral knockings on the base of the mikrokator stand.

A photo of the apparatus arrangement is given in Fig. 12.

I. Sources of error

1. Speedy motion of the pointer

Considerable difficulties were met with in the case that the pointer hitted one of the provided stoppers (graphite): the zero point frequently was altered. In order to avoid this, the pointer has to move slowly when wetting the wire. This was realized by giving the wire a slight inclination from horizontality (say 4°), in order to lessen the strain arising when passing the liquid surface.

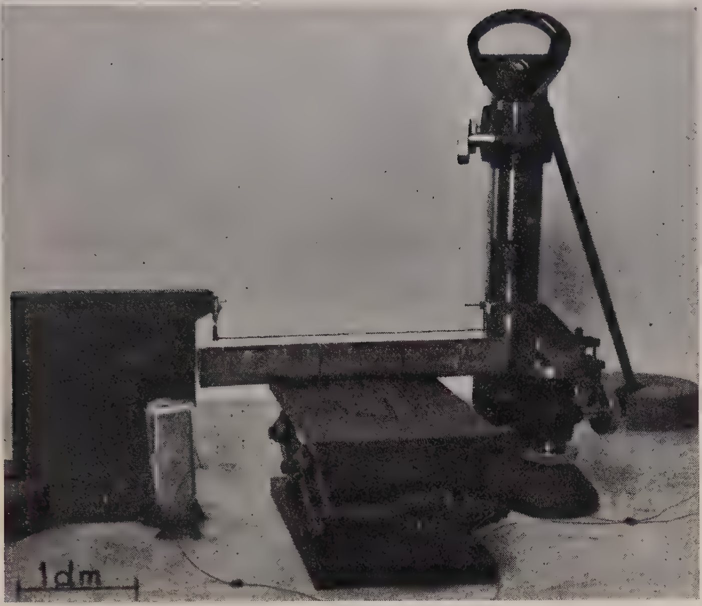

Fig. 12. Photo of apparatus arrangement.

2. Influence of capillary attraction

The capillary attraction between the vertical arm D (fig. 11) and the gable of L, which may arise when the level of the liquid surpasses the wire, might constitute a considerable source of error. It was found, however, that a free distance of 10 mm was sufficient entirely to avoid this influence.

3. Possibility of wire sliding

The method of fixing the ends of the wire demanded much attention, particularly as several results obtained could be explained as the result of some sliding. When using water, "Caulk's Sticky wax" was found suitable, but it could not be used for several solving liquids. Instead the ends were fixed with small brass clamps.

4. Suspected magnetic disturbances

The fact that the adjustable table M contained some iron could possibly exert some influence on the mikrokator (containing itself a magnet!).

In order to elucidate this, a number of blind tests were performed, in which the vessel L was empty. The magnetic influence, if any, would be the same in the absence of the liquid.

The experiments proved that no expansion did occur in the absence of a liquid. Consequently we are justified in considering this source of error to be excluded.

A still better verification was obtained in the following way. The primary condition for the liquostriction to appear is of course that the liquid wets the wire. Now, if the surface of the liquid (water) is covered by a thin layer of lycopode, the wire is not wetted. Actual experiments (3 with $f = 5$ g, 1 with $f = 10$ g) gave no liquostriction whatever ($\Delta l = 0.0$). Hence, even in the case the wire — as in normal tests — is surrounded by a liquid, though not wetting, no effect does appear.

5. Influence of impurities

In all phenomena which depend on a free surface, the purity of this is very important. Hence, in liquostriction experiments, one may expect a plain influence even of very small impurities.

Fig. 13 a (quartz fibre (record No. 34)[1], $d = 0.036$ mm; time against expansion) may serve as a first illustration of the new phenomenon: during a preliminary *dry period* in air only some small variations (due to air currents) are visible. Then comes the *wet period* due to immersion in water; as well seen, there is a *rather uniform expansion,* during about 11 minutes, up to a constant value (about 0.0006 mm; this good constancy may also be attributed to a thermostatic regulation of the room temperature being introduced). After lowering the water level, a contraction sets in immediately.

It may be remarked, that the new dry ("drying") value is lower than the initial one (returning to this after about 12 minutes).

This variation in the position of the dry value does not occur in most irreprochable experiments, and the conclusion was drawn, that in the present case the water must have been *contaminated,* say by some oily substance.

In another test where the contamination probably was still greater, the result Fig. 13 b was obtained.

In this case, the wetting will be seen to proceed much slower — as is generally the case when a considerable contamination is present. The dry value is somewhat lower than in Fig. 13 a.

In order to make matter quite clear, the water surface was now artficially contaminated with some clock oil. The result is to be seen in Fig. 13 c, two items being of particular interest. The expansion which corresponds to the liquostriction is considerably lower than in the previous cases. Further, the contraction setting in on "drying" is much greater than previously, though returning in about the same time.

The present low value of the liquostriction is obviously due to the presence of the oil. The interesting consequence would be this. While *water* causes an expansion of the quartz fibre ("positive liquostriction"), it may be admitted that the *fat oil causes a contraction* ("negative liquostriction").

This represents a remarkable analogy with a result which was obtained in the study of the wetting effect: as a matter of fact, it was found (see Fig. 4) that *fat oils do cause a wetting effect opposite to that caused by most normal liquids*, as water.

A similar test, where the liquid, benzene, was contaminated by clock oil, is to be seen in Fig. 13 d. In spite of the considerable mutual solubility, the

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[1] Series (records) No. 1—33 are only preliminary. A few of the final observations (34—95) have been rejected, due to lacking temperature control or to some (undesired) contamination.

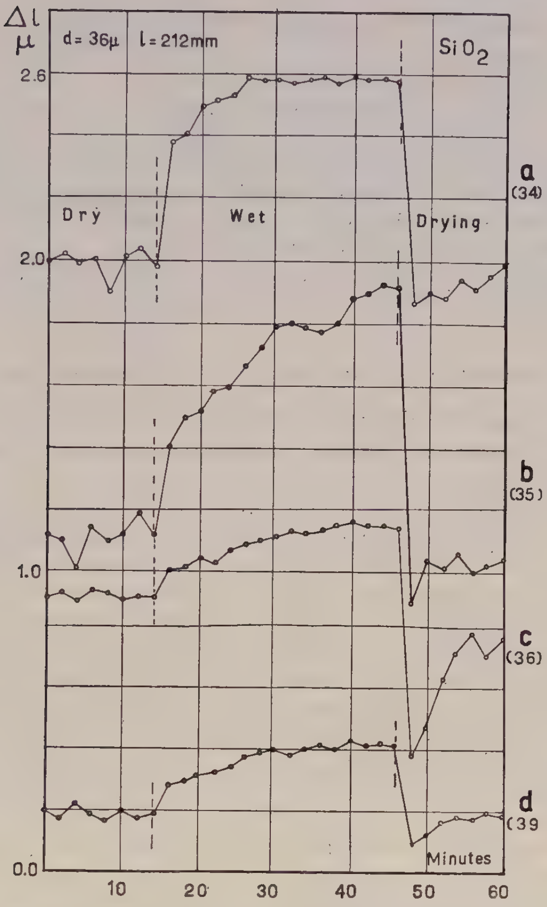

Fig. 13. Liquostriction in quartz fibre (time against expansion Δl). Dry period, wet period, "drying" period. a. Expansion up to constant value; water. On drying, contraction sets in immediately, to a drying value, lower than the initial dry value. Finally, slow increase to the initial value — probably the water was slightly contaminated with oil. b. Expansion takes place much slower; drying value lower than in a. — Slightly greater contamination of the water than in a. c. The expansion is strongly reduced; contraction on "drying" much stronger than previously. — The water had purposely been contaminated with some clock oil. d. Strongly reduced expansion; contraction likewise reduced. — The liquid was benzene, to which some clock oil had been added. — Result corroborates a and b.

conditions are rather similar: the wet value is fairly low (as in Fig. 13 c; benzene gives a lower value than water, and the oil exerts its depressive effect).

It is interesting that this depressive effect of the oil is successively reduced, during the final "dry" period. The reason probably is that the fibre, having passed through the surface into the air, is coated with a thin layer of the oil-containing liquid. This may first, on evaporation, give a continuous oil layer which exerts a fairly strong depressing or contractive effect. Later on, it will form an unduloïd and finally separate drops, which exercise only a weak influence. This last period might be seen best in Fig. 13 c.

It follows from this, that the presence of impurities may constitute a very serious source of error.

6. Temperature control

The attempts to obtain a reliable temperature control were not successful (cp. p. 4). "Thermistors" were not found to be sensitive enough, without a complicated amplifier arrangement not being available. (Unfortunately, we did not dispose of any sufficiently sensitve relay.)

As, in preference, quartz and invar wire were used, the lack of an accurate temperature control was not of a primary importance (cp. further p. 430).

7. Inconstancy of the tension *f* of the instrument used

Every determination of the liquostriction presumes a definite knowledge of the tension of the wire. As already pointed out (p. 419), the tension of the mikrokator could be set at definite values.

Now, even after consideration of all the sources of error, certain variations were found to occur. It was concluded, that these variations could be attributed to accidental irregularities of the tension of the instrument used.

An investigation was made as follows. The instrument was set at a definite tension — under a weak knocking, which should correspond to the inevitable disturbances from the traffic. After some time, a new setting was made, whereby generally, for equilibrium, some weight had to be removed, and so on. Fig. 14 shows that a tension of 5.3 gram (and probably higher) gives a very good constancy (during 32 hours); during the first two hours, however, a decrease of about 10 % occurred. In the case of a tension of 4.3 g, this lowering was found to continue — during the 10 hours observed amounting to 40 %.

At 3.3 g the observations are rather few, but they show, that the decrease, first, is considerable; further it will be seen that during 40 hours (holiday without any knocking) some decrease has taken place. The two last points show a considerable decrease.

At 1.3 g it will be seen (Fig. 14) that the lowering is still considerable: during 3 hours 60 %.

These observations show that great care must be used: this source of error might be a serious one.

In order to avoid the variability of the tension — with kind permission of the company — we substituted the mikrokators (elastic and magnetic) spring arrangement by a new, purely elastic one, working practically without any friction and hence giving constant tension. This new feature however, could not be used, as the expansion sensitivity was insufficient (on account of no astatic arrangement having been provided, as that used in the sensitive mikrokators).

In the meantime, a fairly sensitive (much simpler) lever apparatus was made with a variable weight load. Hitherto, only one liquostriction experiment has, been performed (on copper, by O. Tenow); this, however gave an expansion when immersed in water of the same order as that of the mikrokator tests.

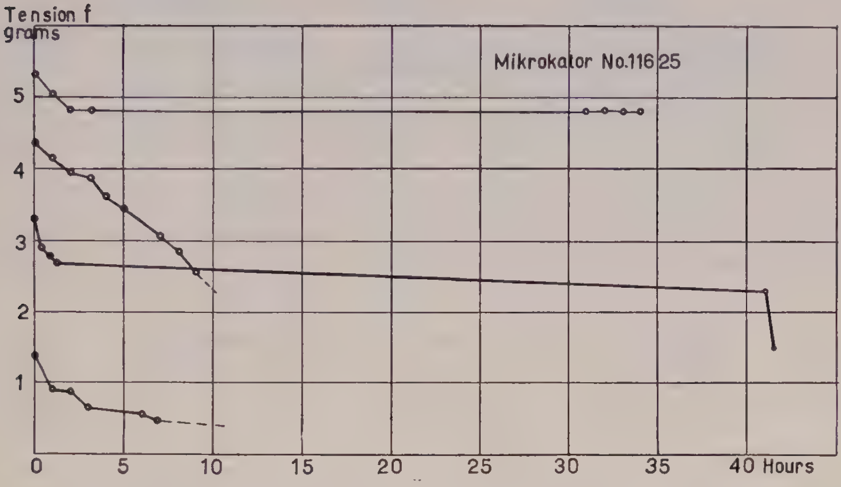

Fig. 14. Observations of the variability of small tensions f in the instrument used.

Messrs. C. E. JOHANSSON have recently been kind enough to place at our disposal a new kind of mikrokator, where the tension may be kept strictly constant ("Surface Balance"). Time has not permitted its perusal.

Summing up: the present source of error might be in itself a serious one: the actual experience gained in experiments repeated with varying tension f (Figs. 17, 23, 29 and 30) afforded evidence that actually *reproducibility exists independently of the f used.*

m. Main observations

When wetting with pure water (recently distilled) almost without exception, a *length increase was obtained*, as was actually expected for "liquostriction".

1. Quartz fibre

The above preliminary experiments Figs. 13 a–d were made with a quartz fibre, but the main object was the influence of impurities. We now have to examine the main quartz experiments.

Fig. 15 — one of the earlier tests — gives a typical example (diameter $d = 0.036$ mm; length $l = 212$ mm; tension $f = 10$ g; temp. $t = 20.5°$ C; $\Delta l = 0.0012$ mm, $\Delta l/l = 4.8 \cdot 10^{-6}$). The slowness of the expansion up to the final value, is probably due to the wellknown fact that *wetting demands a considerable time*, when the object has been long preserved in air (an oily film will of course act in the same direction). Fig. 16 gives evidence that for a fibre ($d = 0.028$ mm, $l = 249$ mm, $f = 5$ g) which had been dry only for a short period before the test, the liquostriction assumes very quickly its final value (the slight difference in the experimental parameters does scarcely influence this result).

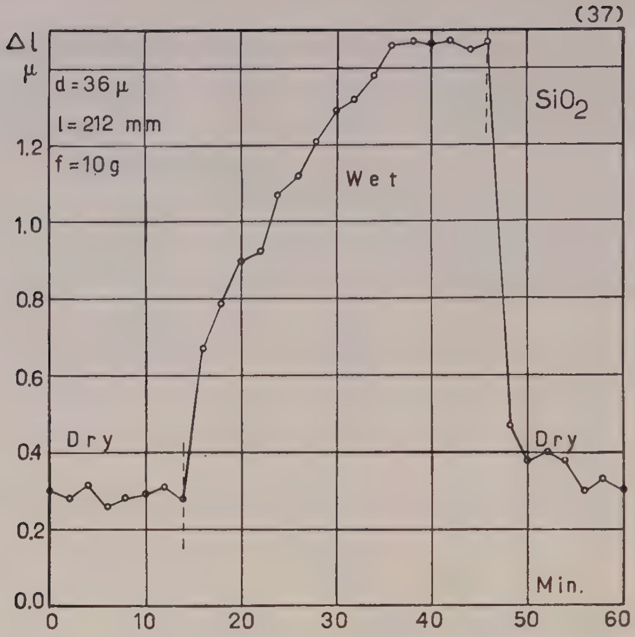

Fig. 15. Liquostriction in a (well dried) quartz fibre. — Wetting progresses slowly (adsorbed air).

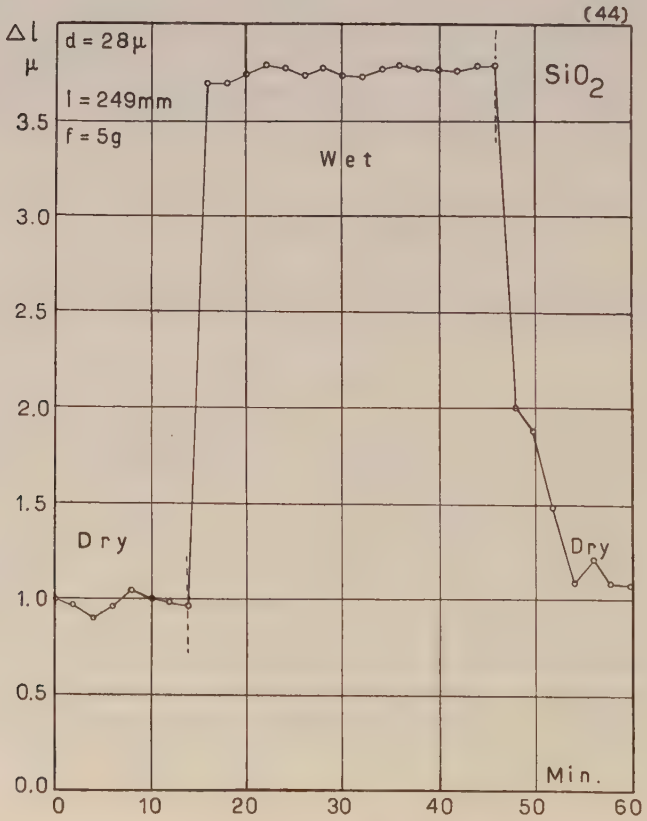

Fig. 16. As Fig. 15, but quartz fibre, having been recently wetted, is quickly moistened (air removed by earlier wetting).

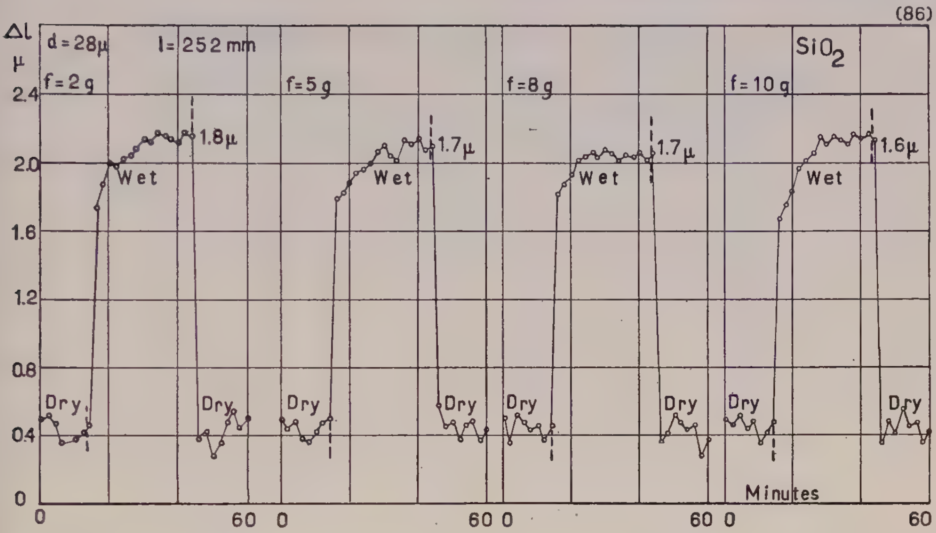

Fig. 17. Liquostriction in a quartz fibre, giving evidence of a good reproducibility, in spite of varying tensions *f*.

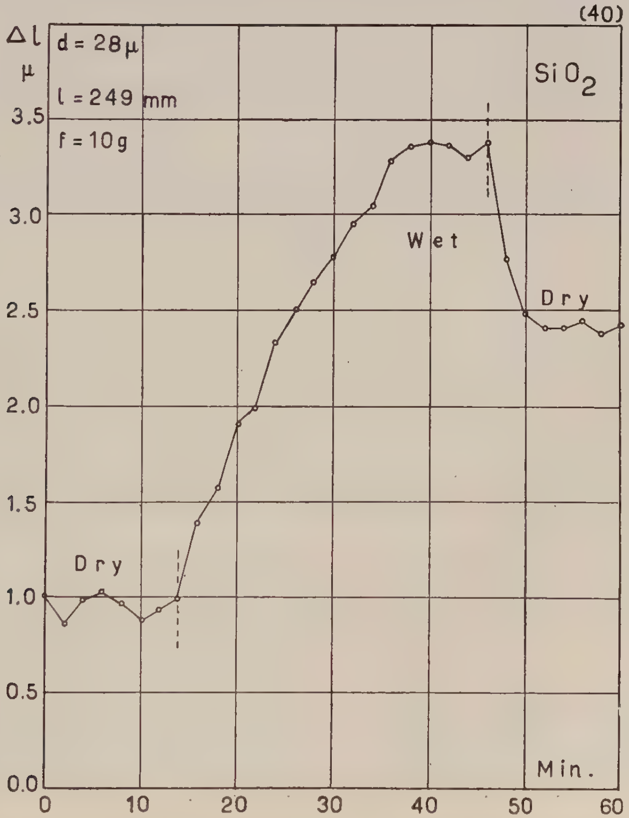

Fig. 18. Liquostriction in a quartz fibre, at $f = 10$ g. — Apparent permanent expansion (sliding?).

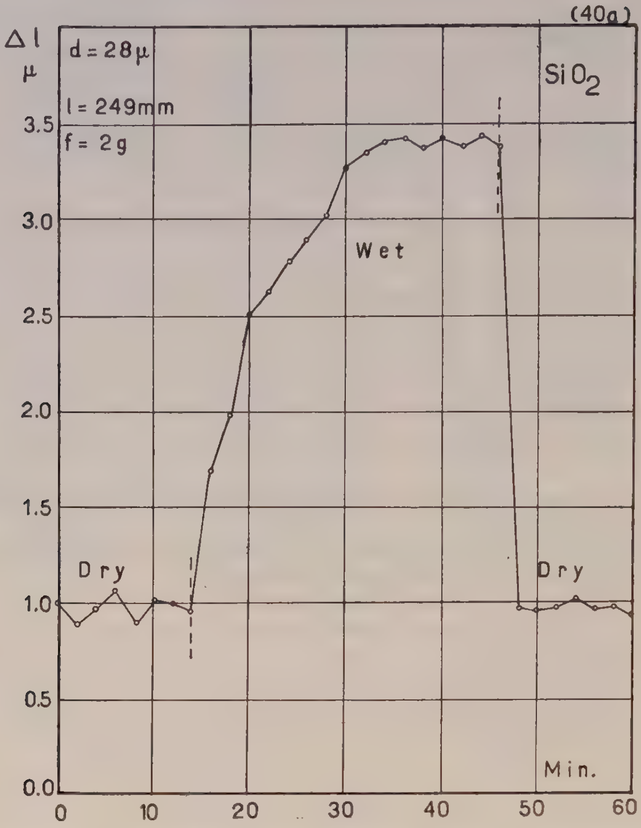

Fig. 19. Liquostriction in the same quartz fibre at $f = 2$ g. — No permanent expansion (no sliding?).

The effect was expected to depend on the tension f used in the mikrokator (see p. 424). In order to examine this, tests were made on a fibre ($d = 0.028$ mm) at tensions $f = 2, 5, 8, 10$ g (Fig. 17). It will be seen, that the influence of variations in f are surprisingly small: the increase in Δl (from 1.6 to 1.8. 0.001 mm, which could be traced as corresponding to a decrease of f from 10 to 2, is of the same order as the experimental errors; thus these four determinations could just as well be given as an *evidence of reproducibility*, independent of the tension.

Another at least apparent influence of the tension used is this. The *dry values* obtained before and after the wetting of the wire are generally equal, as may be seen in Fig. 17 (even in the case of the highest tension, $f = 10$ g). In some cases, however, as evidenced by Fig. 18, the last dry value is considerably higher than the first one: the wire seems to have been elongated during the wet period. In order that the initial dry length should reappear, it was necessary to diminish the tension. With $f = 8$ g the new dry length was 0.0075 mm longer than originally; with $f = 7$ g it was only 0.003 mm longer than originally. With $f = 2$ g the original dry length reappeared, as evidenced by Fig. 19.

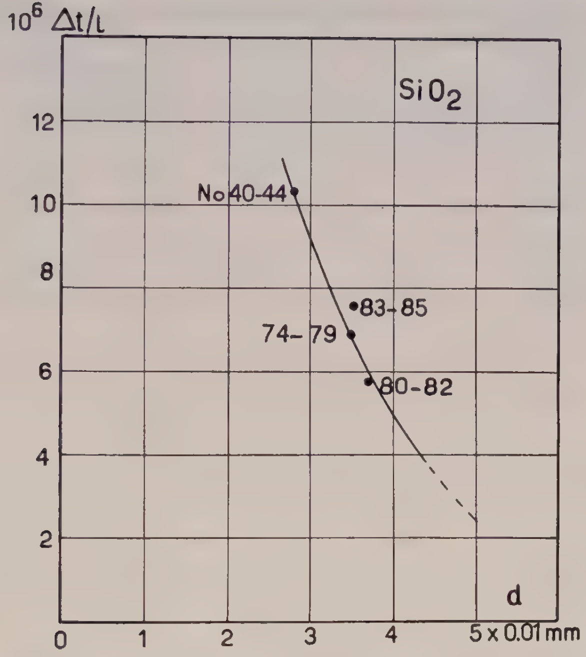

Fig. 20. Relation between liquostriction and diameter *d* of the quartz fibre.

The nearest explanation seems to be that a *small sliding* has taken place successively during the wet period. From some reasons this assumption seemed improbable; it is not possible however to decide the matter at present.

2. Influence of the diameter of the fibre

The basic question regarding the influence of the diameter has not been well treated (sufficiently thick quartz fibres were not available), but some conclusions are possible.

In Fig. 20, where abscissae are diameters of the fibre and ordinates the relative expansion $\Delta\, l/l$, four average values have been plotted.

It will be seen that these values are situated along a slightly bent curve, giving evidence that the liquostriction *increases considerably with decreasing diameter.*

Supposing permissible to extrapolate the curve towards increasing *d* (dotted curve), a fibre $d = 0.050$ mm would correspond to $\Delta\, l/l = 2.5 \cdot 10^{-6}$.

It may be added, that the diameters were determined microscopically and that the sections appeared reasonably circular.

3. Different metals or alloys: invar, Pt, Fe, steel, Ni, Cu. — Conclusion

Next to quartz fibre, it is natural to investigate *invar*, being likewise fairly insensible to temperature variations. An invar wire of diameter $d = 0.050$ mm

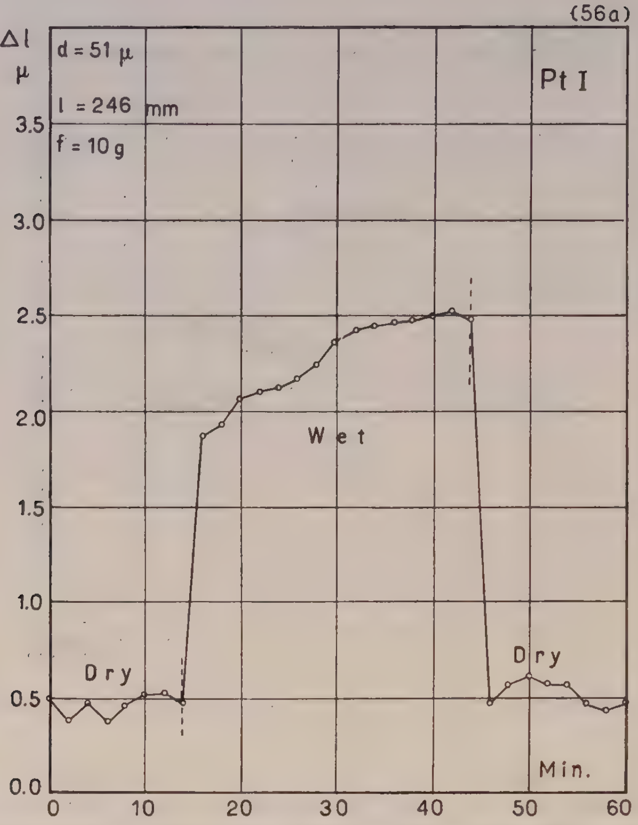

Fig. 21. Liquostriction in cold-drawn (air-dried) platinum, Pt I. Wetting takes place successively.

was kindly presented by professor P. CHEVENARD, Imphy. It has been tested in the primary condition. Though the wire was not well straightened, the liquostriction values were rather uniform (6 tests gave: $10^6 \cdot \Delta l/l$ = 6.1, 6.9, 5.9, 6.5, 7.6, 6.4, in average 6.6. Tensions 5–10 g). — The appearance of the curves was similar, say, to Fig. 25 (Fe).

For *platinum* Fig. 21 shows a typical liquostriction curve (Pt in cold-drawn state, Pt I). The (three) last determinations made — where the temperature uniformity was comparatively satisfactory — gave an average of $\Delta l/l = 7.5 \cdot 10^{-6}$. Fig. 22 was obtained with the same Pt I-wire after a dry period of only 15–20 minutes. It will be seen that the wetting takes place much quicker than in Fig. 21. The temperature control, however, was not very satisfactory. Later on the same wire was investigated, in an air-annealed condition (Pt II; beginning red heat) and under better temperature control. Actually, using one thermo-couple in the liquid and another close to the side of the wire, in conjunction with a Dewar vessel with well known temperature (Hg-thermometer!), it was possible to obtain a fairly good temperature equality between wire and liquid. The average temperature may be estimated to 20.5°, C — as in most of the following cases.

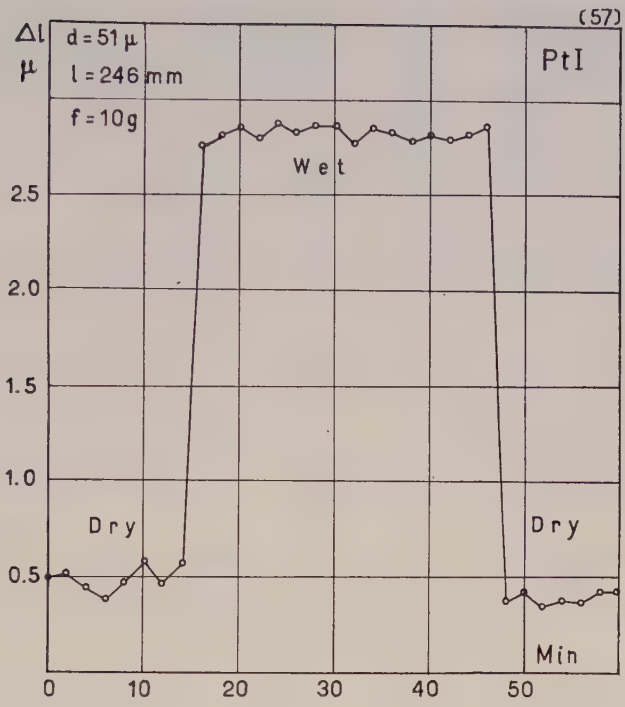

Fig. 22. Liquostriction in Pt I, recently wetted. Wetting takes place at once.

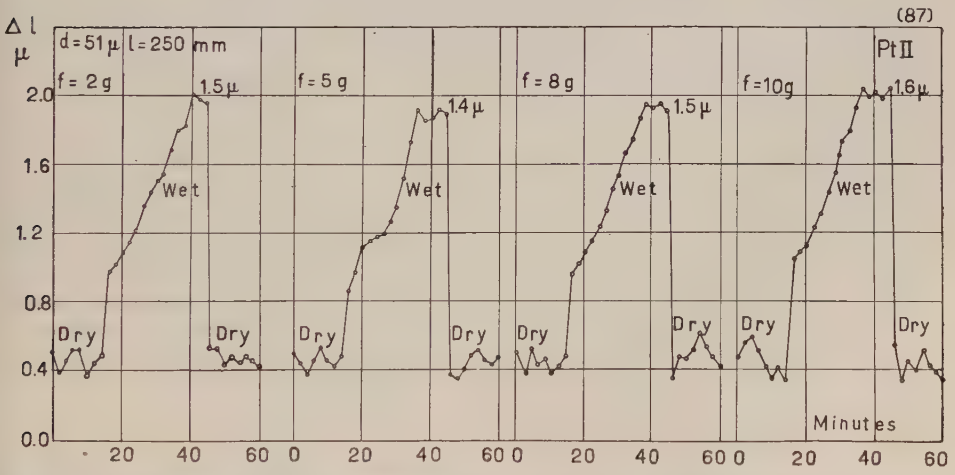

Fig. 23. Liquostriction in Pt II (annealed in air). In spite of different tensions f, the Δl are remarkably constant. The wetting takes place slowly (in spite of short intervening dry periods). This proves that the air adsorbed at high temperature is much more stable than that adsorbed at room temperature.

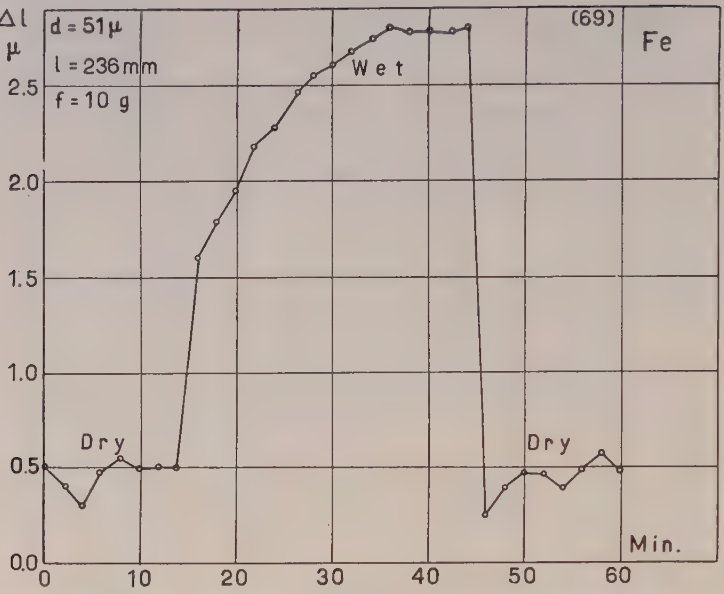

Fig 24. Liquostriction in an iron wire, in H_2O. Wetting comparatively slow. This may be due to adsorbed air or traces of oil.

In Fig. 23 are plotted four series, made on Pt II, at $f = 2, 5, 8, 10$ g. In spite of the different f, the Δl are remarkably constant.

Interesting is the shape of the curves, showing repeatedly a rather *slow wetting* in spite of the successive previous wettings. This differs from the behaviour of Pt I in Fig. 22, where the wetting took place immediately, after the same brief dry period. This is exactly the same behaviour as that shown by quartz (see Figs. 15, 16). It follows from this that the air adsorbed at ordinary temperature (Pt I) must be easily removed by water, while *the air adsorbed at high temperature* (Pt II) *obviously possesses a much more stable character.*

This may be explained by the fairly natural assumption, that the air *penetrates deeper* in the metal at higher temperature than at lower.

In Fig. 24 is plotted a series observed on an *iron* wire $d = 0.051$ mm. The wetting is seen to take place rather slowly. This may be ascribed to adsorbed air, but also to the presence of some oily substance: the shape of the second dry period (showing a definite increase), speaks in this direction (cp. 4 *l* 5, p. 422).

Fig. 25 gives the same iron wire having been preserved (only) 3 hours in a dry condition before the wetting. It will be seen, that the wetting now takes place much quicker than in Fig. 24; likewise in this case, the shape of the second dry period intimates the presence of some oily substance.

Fig. 26 shows the same wire wetted with ethanol. The wetting speed is very great, as may be expected.

It is worthy of remark that even in the case of ethanol the dry afterperiod shows a considerable increase — as in the case of water. This may be easily explained: the wire being wetted by an oil solution in ethanol — though diluted —, on drying the oily substance will remain as a thin coating, which finally contracts into separate drops.

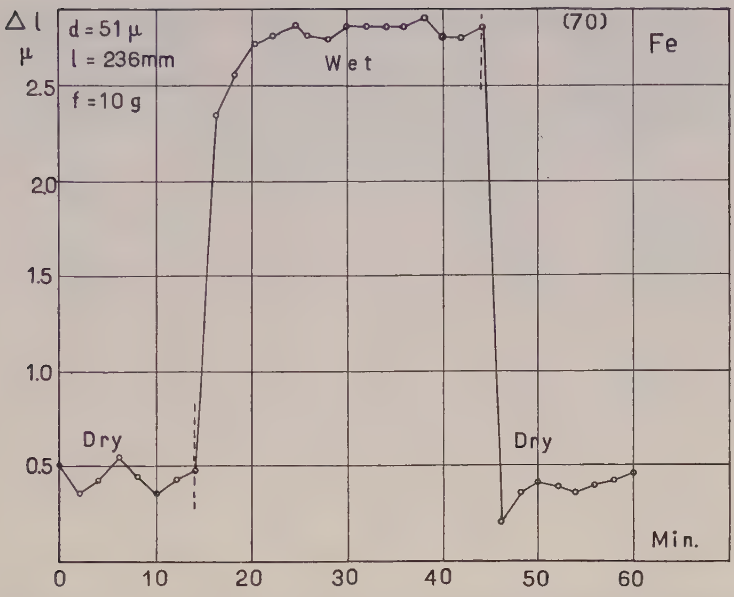

Fig. 25. Liquostriction in the same iron wire, after the (relatively short) dry period of 3 hours. Wetting takes place quickly.

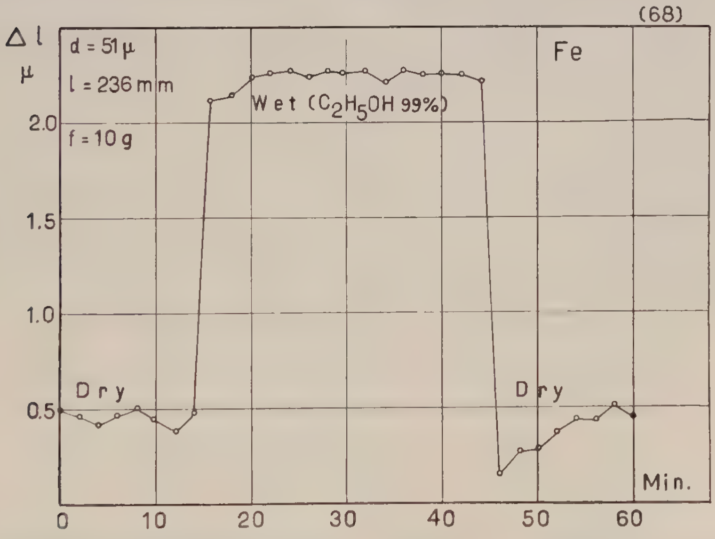

Fig. 26. Liquostriction in the same iron wire, in ethanol; Δl smaller than in H_2O. Wetting takes place very fast. (Dry afterperiod suggests presence of some oil.)

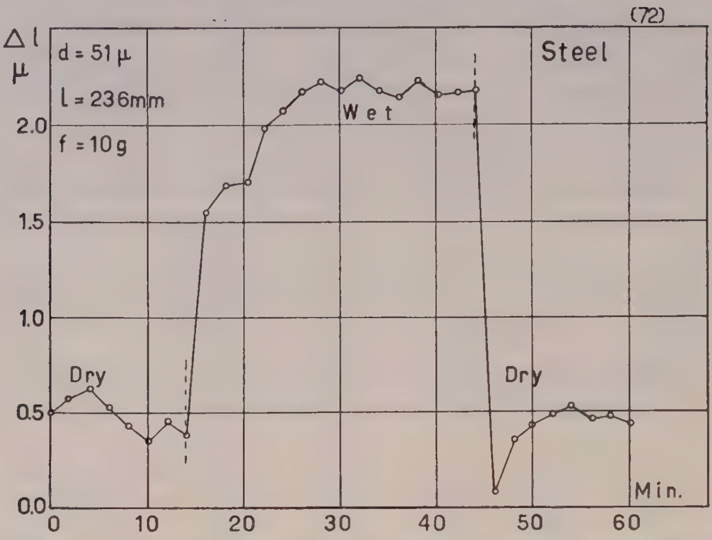

Fig. 27. Liquostriction in a steel wire, in H_2O. (Afterperiod suggests oily contamination.)

Fig. 27, referring to a *steel* wire (about 1 % *c*; $d = 0.051$ mm) is rather similar to the iron in Fig. 24, but the liquostriction appears to be somewhat smaller (7.2 instead of 10).

The same wire in ethanol is to be seen in Fig. 28: the liuqostriction is decidedly smaller than in water. The shape of the dry afterperiod indicates even here a contamination of the liquid.

Fig. 29 gives the result of the tests made on a *nickel* wire ($d = 0.051$ mm, in water). In spite of the different tensions used ($f = 2, 5, 8, 10$ g) the liquostrictions obtained show a great uniformity.

The shape of the curves show a fairly slow wetting, very similar to that of Pt II (in Fig. 23).[1]

The final figure, Fig. 30, reproduces one of four rather similar and regular series made on *copper* in water.

Two kinds of copper were used: the one "ironfree" (drawn in saphir for galvanometers), the other ordinary electrolytic Cu (drawn in steel); both were tested in primary state and also annealed (in vacuo).

These tests (16 in number) gave the following average values:

Table 3

Copper	*d* mm	Unannealed	Annealed	Mean
"Fe-free"	0.053	6.2	8.2	7.2
"Electrolytic"	0.051	7.7	8.4	8.1
		6.9	8.3	7.6

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[1] It may be pointed out that Pt and Ni are both known as active contact substances. (The same is valid for copper.)

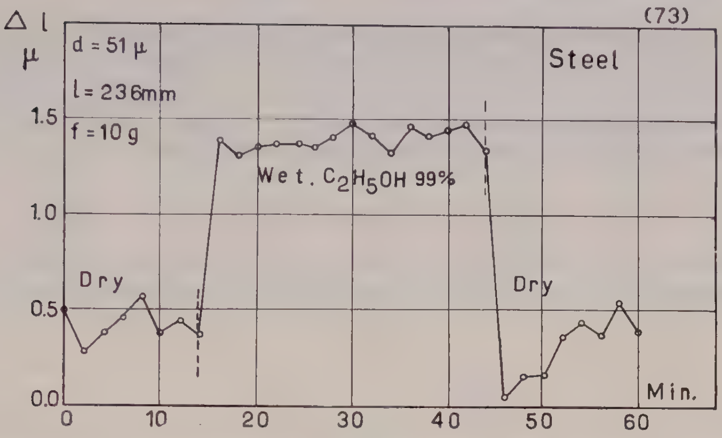

Fig. 28. Liquostriction in the same steel wire, in ethanol. Fast wetting. Δl (as in Fig. 26) less than in H_2O. (Afterperiod suggests contamination.)

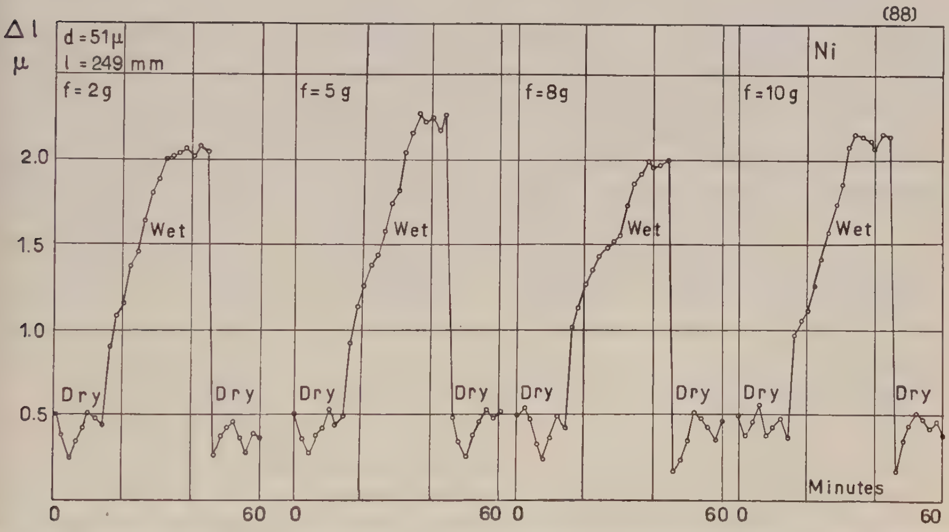

Fig. 29. Liquostriction in a nickel wire, in water. Reproducibility fairly good, in spite of varying tensions f. Wetting rather slow as, say, in Fig. 23.

It will be seen, that the annealed specimens show a slightly higher liquostriction than the unannealed ones. This is the contrary of what was found to be the case for Pt, where after annealing the liquostriction vas considerably lowered. It must be considered, however, that for Pt the annealing was made in air, while for Cu it was made in vacuo; hence a gas occlusion is scarcely to be admitted for Cu.

For the purest Cu, the average liquostriction (7.2) is slightly lower than for the ordinary one, containing some iron (8.1). This might be related to the fact that Fe has shown a somewhat higher value (about 10) than Cu (7.2). Analytically, the amount of Fe in the Cu no doubt is very slight, but it must be remembered that the Fe generally is due to the use of steel draw plates; consequently *the Fe must be localized in the surface of the Cu wire, and may exert a comparatively great influence on any surface phenomenon.*

Conclusion

The different values obtained using *water* are compiled in the following table (where provenience of the wires and observation (record) numbers are also given).

Table 4

Liquostriction in water.

Substance	Provenience	Observ. No.	Diameter d mm	$\frac{\Delta l}{l} \cdot 10^6$	Mean
Quartz fibre......	Heraeus	80—82	0.037	5.7	—
» » (extrap.)	»	—	(0.05)	(2.5?)	—
Invar	Imphy	45—50	0.050	6.6	6.6
Pt I	Heraeus	51—59	0.051	7.5	6.7
Pt II air annealed	»	87A—D	»	6.0	
Fe	Hartm. & Br.	69	0.051	9.7	10.0
Fe, recently wet ..	»		»	10.2	
Steel (1 % C)	Hartm. & Br.	71—72	0.051	7.2	7.2
Ni	Hartm. & Br.	88A—D	0.051	7.2	7.2
Cu, "Fe-free"					
unannealed	Hartm. & Br.	91	0.053	6.2	7.2
vacuo-annealed ..	»	92	»	8.2	
Cu, electrolytic					
unannealed		89	0.051	7.7	8.0
vacuo-annealed ..		90	»	8.4	

It is remarkable that all the liquostriction values observed for metallic materials ($d = 0.05$ mm) show rather *small differences* (around $7.7 \cdot 10^{-6}$). As for quartz (SiO_2) where no direct observations for $d = 0.05$ mm are at hand, the extrapolated value, as indicated, seems to be about $2.5 \cdot 10^{-6}$, or *distinctly lower.*

The highest value observed is that for *iron* (in average 10.0). Somewhat lower is the value for steel (7.2). Steel, Ni and Fe-free Cu have given the same figure (7.2), while Cu containing some iron on the surface has given a higher figure (8.0).

Summing up: so far as the present observations go, they indicate that the liquostriction of different elements is a *property subjected to comparatively small variations* — in some way similar, say, to the *atomic heat* (Si = 3.8, O = 4.0; for most metals 6.4[1]).

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[1] W. Nernst, Theoretische Chemie, 6. Aufl. 1909, p. 175.

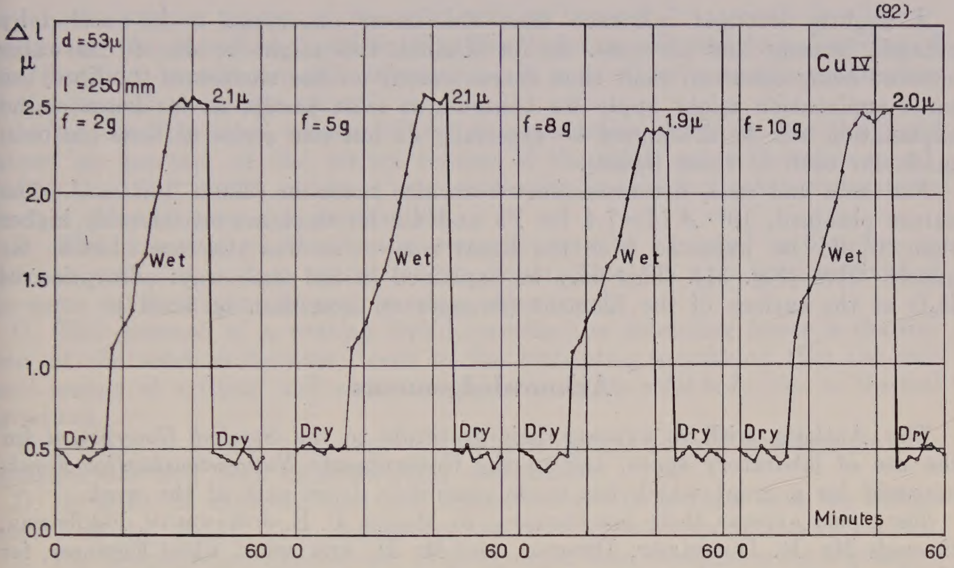

Fig. 30. Liquostriction in a copper wire (Fe-free, annealed in vacuo), in water. Cp. Table 3.

4. Influence on liquostriction of the surface tension of the liquid

Finally, as for the conclusion D (p. 419), implying the influence of the surface tension of the liquid used, some tests have been performed on *quartz* fiber ($d=0.036$ mm, $l=231$ mm, $f=10$ g). Fig. 31 shows the results for the liquids used.

It is obvious that the liquostriction *depends on the surface tension of the surrounding medium. It has the greatest value observed for water* (73 dyn/cm). Ether and xylene were found to *lie on the straight line through H_2O.*

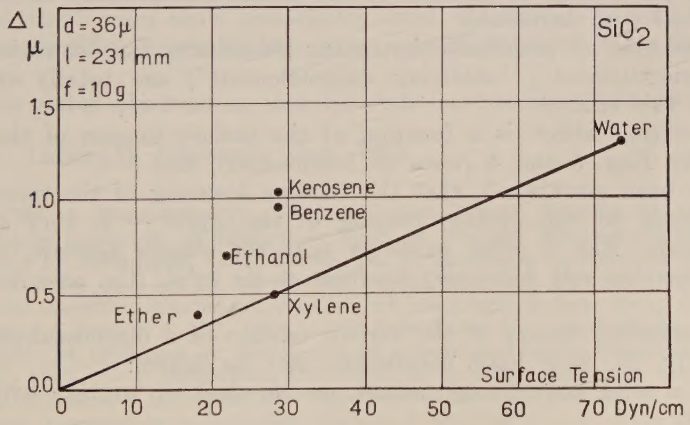

Fig. 31. Relation between liquostriction and surface tension of the wetting medium.

A slightly stronger influence than the linear one seems to be exerted by ethanol, benzene and kerosene. As for ethanol, this might be due to its water content being adsorbed (and thus concentrated) on the surface of the fibre; the same explanation might apply for benzene, at least partly; as for kerosene, no explanation will be attempted — especially as but one series of tests has been made for each of these liquids.

For *iron and steel*, determinations were also made in ("99 %") *ethanol*. The values obtained, $10^6 \cdot \Delta\, l/l = 7.4$ for Fe and 4.2 for steel, are considerably higher than would be expected from the linear rule — as was the case likewise for quartz fibre (Fig. 31). This may be explained in the same way: adsorption of H_2O at the surface of the filament (stronger on iron than on steel?).

Acknowledgements

The Authors wish to express their gratitude to the *Swedish Government* for the use of laboratory space, and to the Governments *Naturvetenskapliga Forskningsråd* for a grant which has made possible a large part of the work.

They also express their indebtedness to Messrs. C. E. JOHANSSON, Eskilstuna, through Mr. R. DOMELLÖF, Director, and Mr. H. ABRAMSON, Chief Engineer, for kindly placing several sensitive mikrokators to their disposal.

They are also indebted to Professor P. CHEVENARD, Imphy, for the invar wire used, and to Mr. H. LIANDER, Civ. Eng., Västerås, for polystyrene samples, and finally to Mr. O. TENOW, Fil. Lic., for discussion and useful advices. The determinations made on marble and polystyrene are due to Messrs. R. SKORSKI and J. SZYLLER.

SUMMARY

1. "Wetting Effect" (BENEDICKS a. RUBEN (1944) 1945) signifies the fact that the tensile strength of a solid depends on the presence of a liquid medium, wetting the solid (but exerting no proper chemical action). The wetting effect may be "negative", implying a decrease (say 40 % by wetting glass with water), or "positive", implying an increase of the tensile strength (say 28 % by wetting quenched steel with kerosene).

Quite a number of practically important phenomena (as "corrosion fatigue", "caustic embrittlement", "soldering embrittlement") are totally or partly influenced by this effect.[1]

2. The wetting effect is a function of the surface tension of the liquid, as illustrated by Figs. 3 and 4 (tests on lump-sugar), and 5–8.

3. It has been established, that the relative lowering of the tensile strength — proportional to the surface tension of the liquid — is very different for different solids. Fig. 9 gives evidence that the *relative decrease of the tensile strength diminishes with increasing hardness of the solid.* (Cp. also *Summary* 2 h p. 419).

4. An elementary theory of the surface tension of a condensed phase is illustrated by Fig. 10. Four basic conclusions may be drawn:

A. If to a solid body foreign atoms are supplied by wetting with a normal

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[1] Cp. original (Swedish) paper (2 b), where some earlier, similar phenomena are treated.

liquid, the surface tension of the solid will be lowered ("Antonoffs Law", originally for the interface liquid-liquid). This lowering will signify a lowering of the (bending) tensile strength likewise, i.e. it may afford a simple explanation of the "negative wetting effect".

As for the "positive" wetting effect, an explanation would be that the liquid causes an increase of the surface tension of the solid, say in forming an adsorbed thin film on its surface ("monomolecular layer"), but other explanations (surface fissures) may also be possible.

B. This lowering of the tensile strength may be expected in first line to increase with the surface tension of the liquid. This has now been established for some solids (sugar, gypsum, marble, glass, steel).

C. The presence of a wetting liquid, causing the attracting forces in the surface of the solid to decrease, leads to the interesting conclusion that the *intimate contact of a liquid will cause an expansion of the solid body* (due to thermal agitation).

This effect — so far unknown — has been designated as "*liquostriction*"; its existence has now been experimentally established.

D. It must be expected that the liquostriction will increase with the surface tension of the liquid. This supposition has likewise been experimentally verified.

5. The liquostriction experiments (Fig. 11) have been executed using a sensitive mikrokator (C. E. JOHANSSON). The sources of error have been carefully discussed.

The liquostriction may be exemplified by Fig. 15, showing a dry quartz fibre successively wetted by water under expansion and then returning to the dry length, and Fig. 16, showing the rapid expansion of a quartz fibre which has been dry only for a short period before the wetting. Fig. 17 shows the reproducibility obtained.

For a few different diameters of the quartz fibre, Fig. 20 shows the average liquostriction values $\Delta\, l/l$ observed.

For metal wires the effect is quite a similar one (Fig. 21, Pt).

6. The influence of the surface tension of some liquids on the liquostriction of a quartz fibre is illustrated by Fig. 31. This shows a similar (though opposite) linear dependency as that of the surface tension on the wetting effect (Fig. 3).

7. The different liquostriction values $\Delta\, l/l$ obtained with water for different substances ($d = 0.05$ mm) show remarkably small differences (around $8 \cdot 10^{-6}$, cp. Table 4). Quartz fibre, however, has given a decidedly lower value ($2.5 \cdot 10^{-6}$, by extrapolation).

The highest value observed is that for iron (amounting to $10 \cdot 10^{-6}$).

Stockholm, Labor. C. Benedicks, Jan. 1951.

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